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(54) Title: CATALYST FOR POLYMERIZATION AND COPOLYMERIZATION OF ETHYLENE

(57) Abstract: A solid titanium complex catalyst for polymerization and copolymerization of ethylene is prepared by the process comprising: (1) preparing a magnesium solution by reacting a halogenated magnesium compound with an alcohol; (2) reacting the magnesium solution with an ester compound having at least one hydroxyl group and a boron compound having at least one alkoxy group to produce a magnesium composition; and (3) producing a solid titanium catalyst through recrystallization by reacting the magnesium composition solution with a mixture of a titanium compound and a haloalkane compound; and optionally reacting the solid titanium catalyst with an additional titanium compound. The solid titanium complex catalyst for polymerization and copolymerization of ethylene according to present invention exhibits high catalytic activity and can be advantageously used in the polymerization and copolymerization of ethylene to produce polymers of high bulk density, narrow particle size distribution and small amount of fine particles.

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**CATALYST FOR POLYMERIZATION AND COPOLYMERIZATION OF ETHYLENE****Technical Field**

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The present invention relates to a catalyst for polymerization and copolymerization of ethylene. More particularly, the invention relates to a solid titanium complex catalyst for polymerization and copolymerization of ethylene. Embodiments of the catalyst system include a solid titanium complex catalyst supported on a carrier containing magnesium. The catalyst may display high catalytic activity and can produce polymers of high bulk density, narrow particle size distribution and small amount of fine particles.

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**Background Art**

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The polymerization of ethylene is usually carried out in liquid phase in the presence of a solvent such as isopentane or hexane, or in the gas phase. The important factors affecting the polymerization in these processes are: polymerization activity and hydrogen reactivity of the catalyst, bulk density of the resulting polymers, the amount of monomers soluble in the solution, particle size distribution, and the existence of fine particles in the resulting polymers.

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Recently, many methods using titanium-based catalysts containing magnesium have been reported as a catalyst for polymerization and copolymerization of olefin. These catalysts may provide high catalytic activity and produce polymers of high bulk density, and are known to be suitable for liquid phase and gas phase polymerization.

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For example, in using a magnesium solution to obtain a catalyst which may produce olefin polymers of high bulk density, the magnesium solution is prepared by reacting magnesium compounds with an electron donor. Electron donors include alcohols, amines, cyclic ethers, or organic carboxylic acids. The magnesium solution is prepared in the

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presence of a hydrocarbon solvent. A magnesium supported catalyst may be prepared by reacting the magnesium solution with halogen compounds such as titanium tetrachloride. Methods using an alcohol to prepare a magnesium solution are disclosed in US Pat. Nos. 3,642,746, 4,336,360, 4,330,649, and 5,106,807. Also, US Pat. Nos. 4,477,639 and  
5 4,518,706 disclose a method which uses tetrahydrofuran or a cyclic ester as the solvent for dissolving the magnesium compound. Although these catalysts may produce polymers of high bulk density, the catalysts need to be improved regarding catalytic activity. Moreover, the polymers produced by using the above catalysts have broad particle size distribution and contain many fine particles, which can be serious defects in the manufacturing process or  
10 treatment.

To improve these problems, US Pat. No. 4,311,414 proposes a method for preparing a catalyst that can produce polymers with narrow particle size distribution and improved average particle size by blast drying magnesium hydroxide. Also, US Pat. Nos. 3,953,414  
15 and 4,111,835 report the preparation method of catalyst that can produce polymers of spherical form and very large average particle size by blast drying magnesium dichloride hydrate. These methods, however, require additional equipment such as blast drying apparatus and the prepared catalyst has low catalytic activity and the resulting polymers contain very large particles making the melting process of the polymers difficult.

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Therefore, there is a demand for catalysts for polymerization and copolymerization of ethylene which may be prepared by a simple process, have high polymerization activity and hydrogen reactivity. In addition, there is demand for catalysts which may produce polymers with narrow particle size distribution and small amount of fine particles.

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#### **Disclosure of the Invention**

The object of the present invention is to solve the problems of prior art methods as mentioned above, and to provide a catalyst for polymerization and copolymerization of ethylene. More

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particularly, the object is to provide a novel catalyst which has high catalytic activity as required in the polymerization and copolymerization of ethylene to afford high bulk density, narrow particle size distribution and small amount of fine particles to the resulting polymers.

5     **Detailed Description of the Preferred Embodiments**

In an embodiment, a catalyst for the polymerization and copolymerization of ethylene, which has high catalytic activity, and may produce polymers of high bulk density, narrow particle size distribution and small amount of fine particles, may be prepared by the process comprising:

- 10       (1) preparing a magnesium solution by contacting halogenated magnesium compound with an alcohol;
- (2) reacting the magnesium solution with an ester compound having at least one hydroxyl group and a boron compound having at least one alkoxy group to produce a magnesium composition solution; and
- 15       (3) producing solid titanium catalyst by reacting the magnesium composition solution with a mixture of titanium compound and haloalkane compound.

The process for preparing a catalyst for polymerization and copolymerization of ethylene can optionally further comprise:

- 20       (4) reacting the solid titanium catalyst with an additional titanium compound once or more.

The process for preparing the catalyst for polymerization and copolymerization of ethylene will be described below in more detail.

- 25       A magnesium solution is prepared by contacting halogenated magnesium compound with alcohol.

In one embodiment, the magnesium compound may be a halogenated magnesium compound. Types of halogenated magnesium compounds used in the present invention may include the following: dihalogenated magnesium compounds such as magnesium chloride, magnesium iodide, magnesium

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fluoride, and magnesium bromide; alkylmagnesium halide compounds such as methylmagnesium halide, ethylmagnesium halide, propylmagnesium halide, butylmagnesium halide, isobutylmagnesium halide, hexylmagnesium halide, and amylmagnesium halide; alkoxymagnesium halide compounds such as methoxymagnesium halide, ethoxymagnesium halide, isopropoxymagnesium halide, 5 butoxymagnesium halide and octoxymagnesium halide; and aryloxymagnesium halides such as phenoxymagnesium halide and methylphenoxymagnesium halide. These magnesium compounds may be used in a single compound or as a mixture of two or more of compounds. Further, the above magnesium compounds can effectively be used in the form of a complex compound with other metals.

10 Other magnesium compounds include compounds that cannot be represented by a formula, as may occur depending on the production method of magnesium compounds, may generally be regarded as a mixture of magnesium compounds. For example, the following compounds may be used as a magnesium compound: such compounds obtained by reacting magnesium compound with polysiloxane compound, silane compound containing halogen, ester, or alcohol; and such compounds 15 obtained by reacting metal magnesium with alcohol, phenol or ether in the presence of halosilane, phosphorus pentachloride, or thionyl chloride.

In some embodiments, the magnesium compounds may be magnesium halides, especially magnesium chloride or alkylmagnesium chloride, having an alkyl group with 1~10 carbon atoms; 20 alkoxymagnesium chlorides, having an alkoxy group with 1~10 carbon atoms; and aryloxymagnesium chlorides, having an aryloxy group with 6~20 carbon atoms.

The magnesium solution used may be prepared as a solution by dissolving the magnesium compound into an alcohol in the presence or in the absence of a hydrocarbon solvent.

25 The types of hydrocarbon solvents used in the present invention may be aliphatic hydrocarbons such as pentane, hexane, heptane, octane, decane, and kerosene; alicyclic hydrocarbons such as cyclobenzene, methylcyclobenzene, cyclohexane, and methylcyclohexane; aromatic hydrocarbons such as benzene, toluene, xylene, ethylbenzene, cumene, and cymene; and halogenated hydrocarbons such as dichloropropane, dichloroethylene, trichloroethylene, carbon tetrachloride, and chlorobenzene.

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The preparation of a magnesium solution from a magnesium compound may be carried out using an alcohol as a solvent in the presence or in the absence of hydrocarbon solvent such as mentioned above. The types of alcohol may include alcohols containing 1~20 carbon atoms, such as methanol, ethanol, propanol, butanol, pentanol, hexanol, octanol, decanol, dodecanol, octadecyl alcohol, benzyl alcohol, phenylethyl alcohol, isopropyl benzyl alcohol, and cumyl alcohol, and the preferable alcohol may be chosen from alcohols containing 1~12 carbon atoms.

The average size and particle size distribution of the obtained catalysts may depend on the type and amount of alcohol used, the type of magnesium compound, and the ratio of magnesium compound to alcohol. The quantity of alcohol used to obtain the magnesium solution is at least 0.5 mol, or may be about 1.0 ~ 20 mol, or more particularly about 2.0 ~ 10 mol per one mole of magnesium compounds.

During the preparation of a magnesium solution, the reaction of a magnesium compound and an alcohol may be carried out in the presence of a hydrocarbon. The reaction temperature, though may vary depending on the type and amount of alcohol used, and may be at least about -25°C, preferably about -10 ~ 200°C, or more preferably about 0 ~ 150°C. The reaction time may be about 15 minutes to 5 hours, or preferably about 30 minutes to 4 hours.

The magnesium solution prepared in step (1) may be reacted with an ester compound having at least one hydroxyl group as an electron donor, and boron compound having at least one alkoxy group to form a magnesium composition solution.

Among the electron donors, the ester compounds having at least one hydroxyl group include: unsaturated aliphatic acid esters having at least one hydroxyl group, such as 2-hydroxyethylacrylate, 2-hydroxyethylmethacrylate, 2-hydroxypropylacrylate, 2-hydroxypropylmethacrylate, 4-hydroxybutylacrylate, pentaerythritoltriacylate; aliphatic monoesters or polyesters each having at least one hydroxyl group, such as 2-hydroxyethylacetate, methyl-3-hydroxybutylate, ethyl-3-hydroxybutylate, methyl-2-hydroxyisobutylate, ethyl-2-hydroxyisobutylate, methyl-3-hydroxy-2-methylpropionate, 2,2-

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dimethyl-3-hydroxypropionate, ethyl-6-hydroxyhexanoate, t-butyl-2-hydroxyisobutylate, diethyl-3-hydroxyglutarate, ethyllactate, isopropyllactate, butylisobutyl lactate, isobutyl lactate, ethylmandelate, dimethylethyltartrate, ethyltartrate, dibutyltartrate, diethylcitrate, triethylcitrate, ethyl-2-hydroxy-caproate, diethyl bis-(hydroxymethyl)malonate; aromatic esters having at least one hydroxyl group, such as 2-hydroxyethylbenzoate, 2-hydroxyethylsalicylate, methyl-4-(hydroxymethyl)benzoate, methyl-4-hydroxybenzoate, ethyl-3-hydroxybenzoate, 4-methylsalicylate, ethylsalicylate, phenylsalicylate, propyl-4-hydroxybenzoate, phenyl-3-hydroxynaphthanoate, monoethyleneglycolmonobenzoate, diethyleneglycolmonobenzoate, triethyleneglycolmonobenzoate; and alicyclic esters having at least one hydroxyl group, such as hydroxybutyl lactone.

10

The amount of the ester compound having at least one hydroxyl group is 0.001 ~ 5 mol, or preferably about 0.01 ~ 2 mol, per one mole of magnesium.

As a boron compound having at least one alkoxy group, which is used as another electron donor in step (2), the compound represented by the general formula of  $BR^1_n(OR^2)_{4-n}$  (wherein  $R^1$  is a hydrocarbon having 1~20 carbon atoms, or halogen,  $R^2$  is a hydrocarbon having 1~20 carbon atoms, n is an integer between 1 and 3) may be used in some embodiments.

For example, the following compounds may be used: trimethylborate, triethylborate, tributylborate, triphenylborate, methylborondiethoxide, ethylborondiethoxide, ethylborondibutoxide, butylborondibutoxide, phenylborondiphenoxide, diethylboronethoxide, dibutylboronethoxide, diphenylboronphenoxide, diethoxyboronchloride, diethoxyboronbromide, diphenoxyboronchloride, ethoxyborondichloride, ethoxyborondibromide, butoxyborondichloride, phenoxyborondichloride and ethylethoxyboronchloride.

The amount of these compound may be about 0.05~3mol, or preferably about 0.05~2mol per one mole of magnesium.

The appropriate temperature for the reaction of the magnesium solution, the ester compound having at least one hydroxyl group, and the alkoxy boron compound is about 0 ~ 100°C, or more

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preferably about 10 ~ 70°C.

Catalyst particles may be recrystallized by treating the magnesium solution prepared in step (2) with a liquid mixture of a titanium compound represented by the general formula of  
5  $Ti(OR)_aX_{4-a}$ , (wherein R is a alkyl group having 1~10 carbon atoms, X is a halogen atom, and "a" is an integer between 0 and 4) and haloalkane.

Examples of titanium compounds which satisfy the above general formula are: tetrahalogenated titanium such as  $TiCl_4$ ,  $TiBr_4$ , and  $TiI_4$ ; trihalogenated alkoxytitanium such  
10 as  $Ti(OCH_3)Cl_3$ ,  $Ti(OC_2H_5)Cl_3$ ,  $Ti(OC_2H_5)Br_3$ , and  $Ti(O(i-C_4H_9))Br_3$ ; dihalogenated alkoxytitanium such as  $Ti(OCH_3)_2Cl_2$ ,  $Ti(OC_2H_5)_2Cl_2$ ,  $Ti(O(i-C_4H_9))_2Cl_2$  and  $Ti(OC_2H_5)_2Br_2$ ; and tetraalkoxytitanium such as  $Ti(OCH_3)_4$ ,  $Ti(OC_2H_5)_4$ , and  $Ti(OC_4H_9)_4$ . A mixture of the above titanium compounds may also be used. The preferable titanium compounds are those containing halogen, or more preferably titanium tetrachloride.

15

The haloalkane compound may be a hydrocarbon compound having 1~20 carbon atoms, and this compound may be used alone or in the mixture of two or more of the above compounds.

20 Examples of haloalkene compounds include: monochloromethane, dichloromethane, trichloromethane, tetrachloromethane, monochloroethane, 1,2-dichloroethane, monochloropropane, monochlorobutane, monochloro-sec-butane, monochloro-tert-butane, monochlorocyclohexane, chlorobenzene, monobromomethane, monobromopropane, monobromobutane and moniodomethane. The preferable haloalkane compound is  
25 chloroalkane compound.

The appropriate amount of the mixture of a titanium compound and a silicon compound used in recrystallization of a magnesium solution is about 0.1~200 mol, or preferably about 0.1~100 mol, or more preferably about 0.2~80 mol per one mole of magnesium compound. The mixing molar ratio of



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the titanium compound to the silicon compound is approximately 1:0.05 ~ 0.95, or more preferably about 1:0.1 ~ 0.8.

When the magnesium compound solution is reacted with the mixture of a titanium compound and  
5 a silicon compound, the shape and the size of the recrystallized solid matter components greatly depend on the reaction conditions.

So, in order to control the shape of the particles, it may be preferable to produce a solid matter composition by reacting the magnesium compound solution with a mixture of a titanium compound  
10 and a silicon compound at a sufficiently low temperature. The reaction temperature may be about -70~70°C, or more preferably about -50~50°C. After the contact-reaction, the reacting temperature is slowly raised so that sufficient reaction is carried out for the duration of about 0.5 ~ 5 hours at about 50 ~ 150°C.

15 The particles of solid catalyst obtained by the above description may be further reacted with an additional titanium compound. The titanium compound used may be titanium halide or halogenated alkoxy titanium with alkoxy functional group having 1~20 carbon atoms. When appropriate, a mixture of these compounds can also be used. Among these compounds, titanium halide or halogenated alkoxytitanium with alkoxy functional group having 1~8 carbon atoms is appropriate, and  
20 more preferable compound is titanium tetrahalide.

The catalyst prepared according to the process described herein can be used for polymerization and copolymerization of ethylene. In particular, the catalyst can be advantageously used in homo-  
polymerization of ethylene, and also in copolymerization of ethylene and alpha-olefins having three or more carbon atoms, such as propylene, 1-butene, 1-pentene, 4-methyl-1-pentene, or 1-hexene.

25

The polymerization reaction using the catalyst described herein may be carried out by using a catalyst system, which comprises: (I) a solid titanium complex catalyst described herein including magnesium, titanium, halogen, and an electron donor; and (II) organometallic compounds including metals in Groups II or III of the Periodic Table.

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The organometallic compound (II) may be represented by the general formula of  $MR_n$ , wherein M is a metal component in Group II or IIIA of the Periodic Table, such as magnesium, calcium, zinc, boron, aluminum, or gallium, R is alkyl group having 1~20 carbon atoms, such as a methyl, ethyl, butyl, hexyl, octyl, or decyl, and n is the atomic valence of the above metal component. In some  
5 embodiments, the organometallic compound is trialkylaluminum having an alkyl group of 1~6 carbon atoms, such as triethylaluminum and triisobutylaluminum, or mixture thereof. When appropriate, the organoaluminum compound having one or more of halogens or hydride groups, such as ethylaluminum dichloride, diethylaluminum chloride, ethylaluminum sesquichloride, or diisobutylaluminum hydride  
10 can also be used.

The solid titanium complex catalyst component described herein can be pre-polymerized with ethylene or alpha-olefin before using in the polymerization reaction. The pre-polymerization can be carried out in the presence of hydrocarbon solvent such as hexane, at a sufficiently low temperature,  
15 under the pressure of ethylene or alpha-olefin, and in the presence of the above catalyst component and organoaluminum compound such as triethylaluminum. The pre-polymerization, by maintaining the shape of catalyst by surrounding the catalyst particle with polymers, is useful in enhancing the shapes of polymers after polymerization. The weight ratio of polymer to catalyst after pre-polymerization is usually about 0.1:1 ~ 20:1.

20

The polymerization reaction can be carried out by gas phase polymerization or bulk polymerization in the absence of an organic solvent, or by liquid slurry polymerization in the presence of an organic solvent. These polymerization methods, however, may be carried out in the absence of oxygen, water, and other compounds that may act as catalytic poison.

25

In some embodiments, the concentration of the solid titanium complex catalyst (I) in the polymerization reaction system, in liquid phase slurry polymerization, is about 0.001 ~ 5 mmol of titanium atom, or more preferably about 0.001 ~ 0.5 mmol of titanium atom, per one liter of solvent. As a solvent, the following compounds or their mixture can be used: alkanes such as pentane, hexane,

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heptane, n-octane, isooctane, cyclohexane and methylcyclohexane; alkylaromatic compounds such as toluene, xylene, ethylbenzene, isopropylbenzene, ethyltoluene, n-propylbenzene and diethylbenzene; and halogenated aromatic compounds such as chlorobenzene, chloronaphthalene and ortho-dichlorobenzene.

5

In the case of gas phase polymerization, the quantity of the solid titanium complex catalyst (I) is about 0.001 ~ 5 mmol of titanium atom, preferably about 0.001 ~ 1.0 mmol of titanium atom, or more preferably about 0.01 ~ 0.5 mmol of titanium atom, per one liter of the polymerization reactant. The preferable concentration of the organometallic compound (II) is about 1 ~ 2,000 mol of aluminum atom, or more preferably about 5 ~ 500 mol of aluminum atom, per one mole of titanium atoms in catalyst (I).

10

To ensure a high reaction velocity of polymerization, the polymerization reaction may be carried out at a sufficiently high temperature, regardless of the polymerization process. Generally, an appropriate temperature is about 20~200°C, or more preferably about 20~95°C. The appropriate pressure of monomers during polymerization is 1~100 atm, or more preferably about 2~ 50 atm.

15

### Examples

The following examples are included to demonstrate certain embodiments. It should be appreciated by those of skill in the art that the techniques disclosed in the examples which follow represent techniques discovered which function well in the practice of the disclosure herein. However, those of skill in the art should, in light of the present disclosure, appreciate that many changes can be made in the specific embodiments which are disclosed and still obtain a like or similar result without departing from the spirit and scope of the invention.

25

### Example 1

#### Preparation of a solid titanium complex catalyst

A solid titanium complex catalyst component was prepared in the following manner.

- 11 -

(i): Preparation of a magnesium solution

19.0g of  $\text{MgCl}_2$  and 400ml of decane were introduced into a reactor of 1.0l which was equipped with a mechanical stirrer and was purged with nitrogen atmosphere. After stirring at 700 rpm, 120ml of 2-ethyl hexanol was added and the reaction was carried out for three hours at the temperature of 120°C. The homogeneous solution obtained by the reaction was cooled to room temperature(25°C).

(ii): Contacting the magnesium solution with ester having a hydroxyl group, and alkoxy boron compound

To the magnesium compound solution prepared in (i), which is cooled to 25°C, 1.2ml of 2-hydroxyethylmethacrylate and 5.1ml of trimethylborate were added, and the reaction was carried out for an hour.

(iii) and (iv): Treatment with a mixture of titanium compound and haloalkane compound, and treatment with titanium compound

After setting the temperature of the solution prepared in step (ii) to 15°C, a solution of a mixture of 40 ml of titanium tetrachloride and 40 ml of tetrachloromethane were dripped thereto for an hour. After completing the dripping process, the temperature of the reactor was raised to 70°C for an hour and maintained at that temperature for an hour. After stirring, the supernatant liquid of the solution was removed, and 300ml of decane and 100ml of titanium tetrachloride were added to the remaining solid, consecutively. Then, the temperature was raised to 90°C and maintained for two hours. Then the reactor was cooled to room temperature and was washed with 400ml of hexane until free titanium tetrachloride remaining unreacted was completely removed. The titanium content of the prepared solid catalyst was 3.7 %.

Polymerization

A 2 liter high pressure reactor was assembled while hot after drying in an oven. By purging the reactor with nitrogen and evacuating the reactor alternatively three times, the reactor was set to nitrogen atmosphere. Then, 1,000ml of n-hexane was introduced, and after introducing 1mmol of triethylaluminum and solid titanium complex catalyst of 0.02mmol titanium atom, 1,000ml of

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hydrogen was added. The temperature of the reactor was raised to 80°C while stirring at 700 rpm with a stirrer and the pressure of ethylene was set to 80psi, and the polymerization was carried out for an hour. After the polymerization, the temperature of the reactor was lowered to room temperature, and excessive amount of ethanol solution was added to the polymerized substance. The polymers  
5 produced were separated and collected, and dried in a vacuum oven at 50°C for at least six hours to afford polyethylene in the form of white powder.

#### Evaluation

The polymerization activity of the catalyst was calculated as the weight ratio of the polymers  
10 produced (kg) to catalysts used (g), and the bulk density(g/ml) of the produced polymers was measured, and the results are shown in Table 1.

Also, to evaluate hydrogen reactivity, which is the extent of change in molecular weight of produced polymers in accordance as the amount of used hydrogen, melt index(g/10min) was measured  
15 by the method prescribed in ASTM D 1238, and the results are shown in Table 1. In general, melt index becomes large as the molecular weight is small.

#### Example 2

A catalyst was prepared in the same way as in example 1 except that 1.2ml of 2-  
20 hydroxyethylmethacrylate and 7.7ml of trimethylborate were used in step (ii). The titanium content of the prepared catalyst was 3.4%. Polymerization was carried out by using this catalyst in the same way as in example 1, and the results are shown in Table 1.

#### Example 3

25 A catalyst was prepared in the same way as in example 1 except that 1.2ml of 2-hydroxyethylmethacrylate and 7.6ml of triethylborate were used in step (ii). The titanium content of the prepared catalyst was 3.5%. Polymerization was carried out by using this catalyst in the same way as in example 1, and the results are shown in Table 1.

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Example 4

A catalyst was prepared in the same way as in example 1 except that 1.2ml of 2-hydroxyethylmethacrylate and 11.4ml of triethylborate were used in step (ii). The titanium content of the prepared catalyst was 3.4%. Polymerization was carried out by using this catalyst in the same way  
5 as in example 1, and the results are shown in Table 1.

Example 5

A catalyst was prepared in the same way as in example 1 except that 1.2ml of 2-hydroxyethylmethacrylate and 12.1ml of tributylborate were used in step (ii). The titanium content of  
10 the prepared catalyst was 3.9%. Polymerization was carried out by using this catalyst in the same way as in example 1, and the results are shown in Table 1.

Example 6

A catalyst was prepared in the same way as in example 1 except that 1.2ml of 2-hydroxyethylmethacrylate and 18.2ml of tributylborate were used in step (ii). The titanium content of  
15 the prepared catalyst was 3.9%. Polymerization was carried out by using this catalyst in the same way as in example 1, and the results are shown in Table 1.

Example 7

A catalyst was prepared in the same way as in example 1 except that 1.2ml of 2-hydroxyethylmethacrylate and 11.4ml of triethylborate were used in step (ii) as a electron donor, and  
20 40ml of titanium tetrachloride and 20ml of tetrachloromethane were used in step (iii). The titanium content of the prepared catalyst was 4.0%. Polymerization was carried out by using this catalyst in the same way as in example 1, and the results are shown in Table 1.

25

Example 8

A catalyst was prepared in the same way as in example 1 except that 1.2ml of 2-hydroxyethylmethacrylate and 11.4ml of triethylborate were used in step (ii) as a electron donor, and  
20ml of titanium tetrachloride and 40ml of tetrachloromethane were used in step (iii). The titanium

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content of the prepared catalyst was 3.3%. Polymerization was carried out by using this catalyst in the same way as in example 1, and the results are shown in Table 1.

#### Comparative Example 1

5 A catalyst was prepared in the same way as in example 1 except that in step (ii), 2-hydroxyethylmethacrylate and trimethylborate were not used. The titanium content of the prepared catalyst was 3.9%. Polymerization was carried out by using this catalyst in the same way as in example 1, and the results are shown in Table 1.

#### 10 Comparative Example 2

A catalyst was prepared in the same way as in example 1 except that in step (ii), 1.2ml of 2-hydroxyethylmethacrylate was used and trimethylborate was not used. The titanium content of the prepared catalyst was 3.3%. Polymerization was carried out by using this catalyst in the same way as in example 1, and the results are shown in Table 1.

15

#### Comparative Example 3

A catalyst was prepared in the same way as in example 1 except that in step (ii), 2-hydroxyethylmethacrylate and trimethylborate were not used and in step (iii), 60ml of titanium tetrachloride was used and tetrachloromethane was not used. The titanium content of the prepared  
20 catalyst was 4.1%. Polymerization was carried out by using this catalyst in the same way as in example 1, and the results are shown in Table 1.

#### Comparative Example 4

A catalyst was prepared in the same way as in example 1 except that in step (ii), 1.2ml of 2-  
25 hydroxyethylmethacrylate and 12.1ml of trimethylborate were used and in step (iii), 60ml of titanium tetrachloride was used and tetrachloromethane was not used. The titanium content of the prepared catalyst was 3.7%. Polymerization was carried out by using this catalyst in the same way as in example 1, and the results are shown in Table 1.

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Table 1

	Activity (kg PE/mmol)	Bulk Density (g/ml)	MI (g/10min)	Particle size distribution of polymers (wt %)							
				>1100 $\mu\text{m}$	840 $\mu\text{m}$	500 $\mu\text{m}$	250 $\mu\text{m}$	177 $\mu\text{m}$	105 $\mu\text{m}$	74 $\mu\text{m}$	44 $\mu\text{m}$
E1	4.2	0.41	2.6	0.6	3.4	10.8	52.4	21.2	8.4	2.6	0.6
E2	4.3	0.39	2.5	0.4	9.4	16.4	45.2	18.7	6.7	3.2	0
E3	3.8	0.40	2.5	0.2	1.2	12.6	58.2	24.8	2.6	0.4	0
E4	3.7	0.38	2.2	0.3	4.6	9.3	54.8	19.8	6.7	4.5	0
E5	4.4	0.39	2.4	0.8	4.6	8.6	59.4	18.6	7.1	0.9	0
E6	4.3	0.37	2.7	0.5	4.1	10.5	52.8	20.2	11.7	0.7	0
E7	4.1	0.35	2.2	0.2	0.7	16.4	41.4	36.8	1.2	2.1	1.2
E8	4.4	0.37	2.8	1.2	12.1	26.2	38.4	19.4	1.5	0.4	0.8
CE1	3.2	0.30	1.6	0	0.6	0.5	7.6	13.9	24.2	36.2	17.0
CE2	3.4	0.31	1.5	2.2	2.7	2.4	9.4	13.7	12.6	34.2	22.8
CE3	3.3	0.24	0.8	1.6	0.4	1.2	8.6	15.5	38.7	19.4	14.6
CE4	3.1	0.29	1.6	0.7	3.8	5.1	16.2	32.4	22.1	15.5	4.2

\*E: Example, CE: Comparative Example

- 5 As can be seen in Table 1, the catalyst for polymerization and copolymerization of ethylene described herein exhibits catalytic activity higher than that of comparative examples by 20~50%, and the polymers produced by the catalyst described herein have higher bulk density. In addition, the particle size distribution shows that 80% or more particles exist in the range of 177~500 $\mu\text{m}$  and the amount of fine particles are very small. Also, the catalyst shows high reactivity to hydrogen which is
- 10 added to control molecular weight of polymers during polymerization, and provides polymers of high melt index.

### Industrial Applicability

- 15 As described in the specification, by using the catalyst in the polymerization of ethylene and in the copolymerization of ethylene and other alpha-olefin, polymers can be produced with high yield rate due to the high activity of the catalyst, and there may be no need of removing catalyst residue. The polymers produced by using the catalyst may show excellent physical properties such as high bulk density and fluidity, and narrow particle size distribution. In conclusion, the solid titanium complex
- 20 catalyst described herein is very useful as a catalyst for polymerization and copolymerization of ethylene.



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Further modifications and alternative embodiments of various aspects of the invention will be apparent to those skilled in the art in view of this description. Accordingly, this description is to be construed as illustrative only and is for the purpose of teaching those skilled in the art the general manner of carrying out the invention. It is to be understood that

5 the forms of the invention shown and described herein are to be taken as the presently preferred embodiments. Elements and materials may be substituted for those illustrated and described herein, parts and processes may be reversed, and certain features of the invention may be utilized independently, all as would be apparent to one skilled in the art after having the benefit of this description of the invention. Changes may be made in the elements

10 described herein without departing from the spirit and scope of the invention as described in the following claims.

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Claims

What is claimed is:

- 5 1. A catalyst for polymerization and copolymerization of ethylene, prepared by a method comprising:  
(1) preparing a magnesium solution by reacting a halogenated magnesium compound with an alcohol;  
(2) reacting the magnesium solution with an ester compound having at least one hydroxyl group and a boron compound having at least one alkoxy group to produce a magnesium composition solution;  
10 and  
(3) producing a solid titanium catalyst by reacting the magnesium composition solution with a mixture of a titanium compound and a haloalkane compound.
- 15 2. The catalyst of claim 1, wherein the method further comprises reacting the solid titanium catalyst with an additional titanium compound.
- 20 3. The catalyst of claim 1, wherein the ester compound having at least one hydroxyl group is an unsaturated aliphatic acid ester having at least one hydroxyl group, an aliphatic monoester or a polyester having at least one hydroxyl group, an aromatic ester having at least one hydroxyl group, or an alicyclic ester having at least one hydroxyl group.
- 25 4. The catalyst of claim 1, wherein the boron compound having at least one alkoxy group is a compound represented by the general formula of  $BR^1_n(OR^2)_{4-n}$  and wherein  $R^1$  is a hydrocarbon having 1~20 carbon atoms, or halogen,  $R^2$  is a hydrocarbon having 1~20 carbon atoms, n is an integer between 1 and 3.
5. The catalyst of claim 1, wherein the titanium compound is represented by the general formula of  $Ti(OR)_aX_{4-a}$ , and wherein R is a alkyl group having 1~10 carbon atoms, X is a halogen atom, and a is an integer between 0 and 4.

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6. The catalyst of claim 1, wherein the haloalkane compound is a hydrocarbon compound which contains at least one halogen and has 1~20 carbon atoms.
7. The catalyst of claim 1, wherein the amount of the mixture of titanium compound and haloalkane  
5 compound is about 0.1~200mol per one mole of magnesium compound, and wherein the mixing molar ratio of the haloalkane compound to the titanium compound is about 0.05~0.95.
8. A method of preparing a catalyst for polymerization and copolymerization of ethylene, comprising:
- (1) preparing a magnesium solution by reacting a halogenated magnesium compound with an  
10 alcohol;
- (2) reacting the magnesium solution with an ester compound having at least one hydroxyl group and a boron compound having at least one alkoxy group to produce a magnesium composition solution; and
- (3) producing a solid titanium catalyst by reacting the magnesium composition solution with a  
15 mixture of a titanium compound and a haloalkane compound.
9. The method of claim 8, wherein the method further comprises reacting the solid titanium catalyst with an additional titanium compound.
- 20 10. The method of claim 8, wherein the ester compound having at least one hydroxyl group is an unsaturated aliphatic acid ester having at least one hydroxyl group, an aliphatic monoester or a polyester having at least one hydroxyl group, an aromatic ester having at least one hydroxyl group, or an alicyclic ester having a least one hydroxyl group.
- 25 11. The method of claim 8, wherein the boron compound having at least one alkoxy group is a compound represented by the general formula of  $BR^1_n(OR^2)_{4-n}$  and wherein  $R^1$  is a hydrocarbon having 1~20 carbon atoms, or halogen,  $R^2$  is a hydrocarbon having 1~20 carbon atoms, n is an integer between 1 and 3.

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12. The method of claim 8, wherein the titanium compound is represented by the general formula of  $Ti(OR)_aX_{4-a}$  and wherein R is a alkyl group having 1~10 carbon atoms, X is a halogen atom, and a is an integer between 0 and 4.
- 5 13. The method of claim 8, wherein the haloalkane compound is a hydrocarbon compound which contains at least one halogen and has 1~20 carbon atoms.
14. The method of claim 8, wherein the amount of the mixture of titanium compound and haloalkane compound is about 0.1~200mol per one mole of magnesium compound, and wherein the mixing molar  
10 ratio of the haloalkane compound to the titanium compound is about 0.05~0.95.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR02/01178

**A. CLASSIFICATION OF SUBJECT MATTER****IPC7 C08F 4/646**

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC07 C08F, B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean patents and applications for inventions

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5151399 A (Shell Oil Company) 29 September 1992 See the whole document	1-14
A	US 5413979 A (Borealis Holding A/S) 09 May 1995 See the whole document	1-14
A	US 4111835 A (Montedison S.P.A) 05 September 1978 Cited in the application, See the whole document	1-14
A	JP 59-68312 A ( Mitsubishi Petrochem. Co. Ltd) 18 April 1984 See the whole document	1-14

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

\* Special categories of cited documents:

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"&amp;" document member of the same patent family

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**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International application No.

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